

Nanoporous Carbons (NPC):Structure, Applications and Catalytic Nanocrystallization

Henry C. Foley

**Department of Chemical Engineering
The Pennsylvania State University**

Session on Nanomaterial Consolidations and Dispersions
NSF-EC Workshop on Nanomanufacturing and Processing
San Juan, PR

January 5-8, 2002

Introduction.

Converting nanoscience to nanotechnology requires nanoengineering and manufacturing. Although the boundary between nanoscience and nanotechnology is currently blurred because the field is so young, one point is clear. Manufacturing nanomaterials, as opposed to doing nanoscientific discovery, will require the development of well-defined processes with unprecedented dimensional control for the formation and consolidation of nanostructures into functional systems. This transition from science to technology at the nanoscale will be driven by new paradigms in process and catalytic reaction engineering, developed specifically for the production of novel and complex structures that include particles, fibers and lamellae of soft as well as hard materials. For these reasons doing research aimed at the nanoengineering of such new processes and nanomanufacturing techniques in parallel with basic nanoscience is not just interesting, it is necessary.

This paper reviews progress that we have made recently in the fabrication of supported nanoporous carbon (NPC) membranes and catalytic membranes, the simulation of these complex solid structures and the understanding of alkali metal catalyzed nanorecrystallization. The fabrication of a defect-free supported NPC layer structure to produce a high quality membrane is a prototypical process manufacturing problem with many of the same challenges which will be presented by the production of similar and more complex nanosystems. Accurate simulation of the complex geometries of NPCs is a necessity with these materials, but so is the simulation of the layer deposition and pyrolysis process, if we are eventually to be able to analyze and model diffusive transport through them. Finally, new catalytic routes to well-defined nanodomains by the conversion of the "amorphous" structure of NPC opens up the possibility of carrying out solid-solid interconversions as opposed to the usual gas to solid conversions used to produce nanostructures. New lower energy chemical processes or high rate syntheses, (i.e. catalysis), such as this will be as important to the burgeoning nanoprocess technologies as it is to today's chemical and petroleum processing industries.

Manufacturing and Use of Nanoporous Carbon Membranes

Nanoporous carbons are materials which have a narrow range of pore dimensions centered around 0.5 nm. (Slide 4) This makes them ideal membranes for small molecule separations and catalysis. Although they have short range order they have no long range order. (Slide 5) NPC are derived via the pyrolysis of polyfurfuryl alcohol (PFA) in this work. (Slide 6) Membranes are

derived from layers of the NPC supported on porous stainless steel tubes or plates. The polymer is coated on the support with an ultrasonic nozzle to give a high degree of mass flow and location control (Slide 7,8). Pyrolysis is done at 400-600°C under an inert gas flow with constant rotation. Either incomplete coverage or defects brought on by cracking at thicknesses above a critical value (20 microns) will diminish performance. The oxygen to nitrogen ideal selectivity ratio is an excellent measure of defects and is used as such. (Slides 9-11) Simulation of the polymer deposition process on the substrate surface has shown that patterns of deposition and hence layer thickness are highly sensitive to the small changes in control parameters. (Slides 12-13)

Consolidation of these NPC membranes with catalysts either at the membrane surface or within the high carbon matrix, leads to systems which can combine separation and reaction beneficially. For example placing a layer of 12-tungstophosphoric acid on the supported NPC membrane (SNPCM) leads to a material which can completely convert MTBE to methanol and isobutylene (overcoming equilibrium) and simultaneously separate the two products, leaving MTBE on the reaction side of the membrane while methanol is permeated away. (Slides 14-16) Nanoparticles of platinum metal (Pt_x , $d_p \sim 7.0$ nm) may be produced in conjunction with the production of the NPC layer. (Slides 17-20) Hydrogenation of propylene, n-butene and i-butene, shows that the C_3 olefin permeates faster than the two C_4 olefins and that it is nearly completely converted to alkane even at the lower temperatures tested (25-50°C). The i- C_4 olefin permeates faster than the n- C_4 . Perhaps, most interesting is the fact that the intrinsic rate constant for the C_3 is almost 30 times larger than that for i- C_4 olefin and is at least 10 times that for the n- C_4 olefin.

High Rate Solid Synthesis: Catalytic Nanorecrystallization of NPC

Structurally, the NPC materials are one the one hand characterized by the narrow distribution of pores, but they are also glass-like or "amorphous. (Slides 21,22) Lacking long range order but having a regular pore structure, they present a challenge to simulation. However, by using chemical constraints along with physical and chemical properties data, stochastic models can be derived which capture the essential features of these materials. Hence the pores can be considered to be consistent of not just six member rings as found in graphite, but also five and seven member rings which break planar symmetry sufficiently to form the 0.5 nm pores.

Cesium and other alkali metals are adsorbed and absorbed strongly into the NPC materials. (Slide 23) This leads to charge transfer to the polynuclear nanodomains as shown by ESR, XPS and magnetic susceptibility measurements. (Slide 24) When the NPC are heat treated at temperatures as high as 1200°C, they resist graphitization (slide 25). However, in the presence of cesium metal this resistance nearly disappears. For example after treatment at just 50°C with cesium (slide 26), we note the formation of highly unusual nanocrystalline domains consistent of relatively few layers. When we heat treat at 350 and 500°C, we note that the nanocrystalline domains are more numerous, larger in size and consist of many more layers. This suggests that the kinetics of the nanocrystallization process are activated, but the drop in the barrier energy in the presence of cesium, versus the purely thermal reaction, must be very large, since the solid state chemistry now goes at such low temperatures. A part of the thermodynamic driving force for this process is the release of strain energy in the solid. We know from separate calorimetric measurements that the NPC solids are at least 5-10 kcal mol⁻¹ higher in energy than is graphite. As to the mechanism of the nanocrystallization process, we simply do not as yet know it. It must, however, involve the transfer of electrons from the cesium to the carbon lattice. This may be the other part of the thermodynamic driving force. One possibility for the mechanism is that the initial transfer causes a curved to planar transformation in the vicinity of the cesium domains which reduces the charge on the cesium domain and releases strain energy in the carbon solid. This process then may propagate outward from the cesium, further dissipating charge in the cesium and releasing more strain energy from the carbon as it takes place. This propagation process would continue to expand the nanocrystallized domain locally around the cesium domain until the electrochemical potential gradient for electron transfer dissipates to a magnitude which is too small to drive the process further (slide 28) at some distance, r , away from the cesium source.

We now know that all the alkali metals and the sodium-potassium alloy phases do this chemistry, except for lithium. Further work is underway to understand this intriguing solid state catalysis.

Extensions of our current work include the use of these materials for ultrafiltration, for fuel cell catalysis and for catalytic membranes. (Slide 29) We are also pushing back the envelop on the simulation of the complex structures. Perhaps, one of the most intriguing new areas which we are moving into is that of nanoreactor systems for the mass production of polymer nanofibers. We have plans underway to design such nanoreactors and to prototype them here at Penn State in the next twelve months. (Slide 30) Using nanofabrication methods we should be able to fabricate reactors to produce either solid or hollow nanofibers. When composed of polyacetylene, we expect these to convert to carbon nanofibers and tubes under the action of pyrolysis.

Conclusion

To conclude, nanoscience has grown at an explosive pace over the last decade. To convert this science into useful technology requires that we begin to do nanoengineering and development research at a pace which is commensurate with that of nanoscientific discovery. Hence engineers and the funding agencies which support them need to rise to this challenge. (Slide 31) New, high rate - high yield nanoprocesses, nanomanufacturing techniques, metrologies, and process controls are all necessary to produce the complex nanomaterials which will be integrated into nanosensors and nanoactuators and systems of technology.

Bibliography

Strano, M.S. and Foley, H.C. "Temperature and Pressure Dependent Transient Analysis of Single Component Permeation through Tubular Nanoporous Carbon Membranes. *Carbon* (in press).

Strano, M.S., A. Zydney, H. Barth, G. Wooller, H. Agarwal and H.C. Foley. "Ultrafiltration Membrane Synthesis by Nanoscale Templating of Porous Carbon, *Journal of Membrane Science* (in press).

Strano, M.S., and Foley H.C. Synthesis and Characterization of Heteropolyacid Nanoporous Carbon Membranes, *Catalysis Letters* 2001, 74, 177-184.

Strano, Michael S. and Henry C. Foley. "Synthesis and Characterization of Catalytic Nanoporous Carbon Membranes," *AIChE Journal*, 2001, 47, 66-78.

Shiflett, Mark B., John F. Pedrick, Scott R. Mclean, Shekhar Subramoney and Henry C. Foley, "Characterization of Supported Nanoporous Carbon Membranes," *Adv. Mats.*, 2000, 12, 21-25 .

Acharya, Madhav and Henry C. Foley. "Semi-Empirical Analysis of Gas Transport in Nanoporous Carbons Using Transition State Theory," *AIChE Journal*, 2000, 46, 911-922.

Shiflett, Mark B. and Henry C. Foley," Ultrasonic Deposition of High Selectivity Carbon Molecular Sieve Membranes," *Science*, 2000, 285, 1902-1905.

Acharya, Madhav and Henry C. Foley, "Spray-Coating of Nanoporous Carbon Membranes for Air Separation," *J. Membrane Sci.*, 1999, 1-5.

Petkov, Valeri, Remo G. DiFrancesco, , Simon J. L. Billinge, Madhav Acharya, and Henry C. Foley, "Simulation of Nanoporous Carbons: A Chemically Constrained Structure," *Philos. Mag., B*, 1999, 79, 1519-1530.

Acharya, Madhav, Michael S. Strano, Jonathan P. Mathews, Simon J. Billinge, Valeri Petkov, Shekhar Subramoney and Henry C. Foley, "Simulation of Nanoporous Carbons: A Chemically Constrained Structure," *Philos. Mag., B*, 1999, 79, 1499-1518.

